

Ultrasonic studies on interionic interactions of some alkali metal halides in aqueous d-glucose solution at varying molalities and temperatures

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Abstract

The present experimental investigation was carried out in order to explore the possible molecular interionic interactions of alkali metal halides namely, sodium chloride, potassium chloride, potassium bromide and potassium iodide in aqueous D-glucose solution at 303.15, 308.15K and 313.15 K. Experimental values of density (ρ), viscosity (η) and ultrasonic velocities (U) were carried out on the liquid ternary mixtures of water +D-glucose + alkali metal halides. The binary solvent mixture of water + D-glucose was prepared under molality(m) basis say, at two fixed molalities (0.2 and 0.4mol.kg⁻¹). Alkali metal halides (NaCl, KCl, KBr and KI) were added under different molalities with these binary solvent mixtures. The related and relevant parameters correlated to our present study such as adiabatic compressibility (β), molal hydration number (n_H), apparent molal compressibility (ϕ_K), apparent molal volume (ϕ_V), limiting apparent molal compressibility (ϕ_K^0), limiting apparent molal volume (ϕ_V^0) and their associated constants (S_K , S_V), partial transfer volume ($\Delta \phi_V^0$) from water to aqueous solution were determined. In order to stress more on the viscometric data to substantiate its importance, the viscosity B-coefficient has been meticulously evaluated, The present investigation has exploited the possible molecular associations such as ion-ion, ion-solvent, solute-solvent, solute-solute etc., which are identified and eventually discussed about the behaviour of solutes (alkali metal halides) in the solvent mixture.

Keywords: molal hydration number, adiabatic compressibility, structure-maker, viscosity, B- coefficient, transfer volume, limiting apparent molal volume

INTRODUCTION

Saccharides are very important for some physiological processes. They are not only the basic material for energy metabolism in organisms, but also play a significant role in the configuration of biological molecules [1, 2]. The study of carbohydrates/saccharides has become a subject of increasing interest because of the multidimensional physical, biochemical and industrially useful properties of these compounds [3-9]. In addition to their importance in the food, pharmaceutical and chemical industries, simple saccharides have received considerable attention for their ability to protect biological macromolecules [10, 11]. Sugars and polyols are well known stabilizing agents of proteins/enzymes [12, 13] in their native state owing to their ability to enhance the structure of water. Saccharides and their derivatives as the most abundant class of biomolecules are known to exist in wide range of forms, which is a reflection of their biological versatility and the great diversity of their biological functions such as structural, protective metabolic and recognition. The saccharide components of cell membranes are the receptors of biologically active components

(enzymes, drugs, etc). Saccharides are able to stabilize the native state of proteins/enzymes [14-16]. Interactions of electrolytes with saccharides are very important in exploring the stability of polysaccharides in biological systems as well as in the chemical industry of saccharides. It is an essential component for maintaining cell viability, a natural cell-protecting agent, as well as an energy reservoir in many organisms [17]. It has been found that the decomposition, synthesis, metabolism and transmembrane transport of saccharides have relationships with the concentration of H⁺, Na⁺ and other metal ions in body-fluid. So the study of the interaction between alkali metal halides and aqueous D-glucose is valuable to examine the influence of electrolytes on some physiological behavior and helpful to understand the essence of some biological phenomena.

Various thermodynamic [10, 18-19] and spectroscopic [20, 21] studies have shown that the hydration of saccharides depends upon the number of hydroxyl groups [21, 22] the potential hydrogen bonding sites and relative positions of the next nearest neighbour hydroxy groups within the carbohydrate molecules [23]. Jha et al [24] have determined densities and viscosities of some alkali metal chlorides in tetrahydrofuran + water mixtures at different concentrations and temperatures. From the density data, apparent molar volumes have been derived and analysed. Banipal and coworkers [25] have determined apparent molar volumes of some disaccharides in water and in aqueous guanidine hydrochloride solutions at different concentrations and at 298.15 K from density measurements. Partial molar volumes at infinite dilution determined

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from ϕ_v values have been utilized to estimate partial molar volumes of transfer of the disaccharides from water to aqueous guanidine hydrochloride solutions. Parmar and Dhiman [26] have recently reported on the determination of partial molar volumes of some mineral salts from density measurements in aqueous medium at different concentrations and temperatures. The results have been interpreted in term of ion-solvent and ion-ion interactions.

Our earlier literature survey shows that although studies of inter-ionic interactions and viscosities in binary mixtures are abundant, those of ternary systems are few. Taking this in view, we have carried out the present investigation in the light of the following aspects.

- Determination of adiabatic compressibility (β), molal hydration number (n_H) as a function of molal concentration of alkali metal halides namely NaCl, KCl, KBr and KI in aqueous D-glucose solutions at different temperatures (303.15, 308.15 and 313.15 K)
- Determination of apparent molal compressibility (ϕ_K), apparent molal volume (ϕ_v), limiting apparent molal compressibility (ϕ_K^0), and its related constant (S_K), limiting apparent molal volume (ϕ_v^0) and its related constants (S_v), partial transfer volume ($\Delta \phi_v^0$) and
- To shed more details on the viscometric study, viscosity B-coefficient of Jones-Dole equation has also been evaluated.

Experimental

D-glucose (SRL, India) and alkali metal halides, namely NaCl, KCl, KBr and KI (AR, BDH) were dried over P_2O_5 in vacuum desiccators for more than 48h. The reagents were always placed in the desiccators over P_2O_5 to keep them in dry atmosphere. Freshly prepared doubly distilled water (sp. conductivity $\sim 10^{-6} \text{ ohm}^{-1}\text{cm}^{-1}$) was used for preparing the solutions at different concentrations. Aqueous solutions were prepared and used on the day they were prepared. The required quantity of alkali metal halide for a given molality was dissolved in the binary mixture and similar procedure was adapted for different molalities. The chemicals were weighed in an electronic digital balance (SHIMADZU AX-200, Japan Make) with a least count of 0.0001g. The density was determined using a specific gravity bottle by relative measurement method with an accuracy of $\pm 0.01 \text{ kgm}^{-3}$. An Ostwald's viscometer of 10ml capacity was used for the viscosity measurement. Efflux time was determined using a digital chronometer within $\pm 0.01\text{s}$. An Ultrasonic Interferometer having the fixed frequency of 2MHz (Mittal Enterprises, New Delhi-Model: F-81) with an overall accuracy of 2ms^{-1} has been used for velocity measurement. An electronically digital operated constant temperature bath (RAAGA Industries, Chennai) has been used to circulate water through the double walled measuring cell made up of steel containing the experimental solution at desired temperature, whose accuracy is maintained at $\pm 0.1\text{K}$.

RESULTS AND DISCUSSION

Table 1 Values of density (ρ), viscosity (η) and Ultrasonic velocity (U) of alkali metal halides in aqueous D-glucose solution at different temperatures

Molality (mol.kg ⁻¹)	ρ (kg.m ⁻³)		η ($\times 10^{-3} \text{ NSm}^{-2}$)								U (ms ⁻¹)							
			0.2 m		0.4 m						0.2 m		0.4 m					
	Temperature (K)																	
	303.15	308.15	313.15	303.15	308.15	313.15	303.15	308.15	313.15	303.15	308.15	313.15	303.15	308.15	313.15	303.15	308.15	313.15
Sodium chloride + aqueous D-glucose solution																		
0.00	1005.60	1005.01	1004.57	1012.31	1010.62	1008.13	0.9685	0.8832	0.8032	1.0343	0.9377	0.8467	1527.31	1531.96	1536.09	1538.31	1541.63	1544.58
0.05	1010.71	1009.91	1008.67	1017.94	1015.89	1013.13	0.9838	0.8976	0.8161	1.0522	0.9552	0.8683	1533.00	1538.27	1542.11	1544.94	1547.06	1550.76
0.10	1015.96	1014.97	1013.87	1022.83	1021.01	1018.33	0.9988	0.9118	0.8301	1.0686	0.9700	0.8769	1539.10	1544.31	1548.72	1550.26	1553.64	1556.12
0.15	1021.23	1020.07	1019.11	1028.17	1026.42	1023.33	1.0148	0.9262	0.8442	1.0840	0.9847	0.8907	1545.37	1556.48	1554.08	1556.37	1559.53	1562.04
0.20	1026.36	1025.26	1024.41	1033.28	1031.86	1028.73	1.0301	0.9407	0.8583	1.0999	0.9997	0.9056	1551.67	1556.63	1560.44	1562.10	1564.97	1568.33
0.25	1031.18	1030.38	1029.38	1038.56	1036.92	1034.31	1.0450	0.9557	0.8717	1.1156	1.0153	0.9200	1558.14	1562.48	1566.35	1568.04	1570.03	1572.57
0.30	1037.40	1035.99	1034.81	1043.59	1041.19	1039.28	1.0616	0.9705	0.8857	1.1313	1.0292	0.9339	1564.34	1568.54	1572.29	1574.35	1576.81	1578.91
Potassium chloride + aqueous D-glucose solution																		
0.00	1005.60	1005.01	1004.57	1012.31	1010.62	1008.13	0.9685	0.8832	0.8032	1.0343	0.9377	0.8467	1527.31	1531.96	1536.09	1538.31	1541.63	1544.58
0.05	1011.45	1010.01	1009.09	1020.81	1018.41	1017.11	1.0051	0.9296	0.8703	1.0691	1.0010	0.9288	1532.48	1536.02	1541.14	1543.01	1546.47	1549.36
0.10	1016.53	1015.13	1014.88	1025.93	1023.51	1022.31	0.9998	0.9246	0.8659	1.0645	0.9962	0.9241	1537.18	1540.84	1545.92	1547.71	1551.31	1554.14
0.15	1022.34	1020.83	1019.15	1031.78	1028.78	1027.71	0.9952	0.9201	0.8599	1.0597	0.9912	0.9195	1541.89	1545.68	1550.68	1552.43	1556.17	1558.90
0.20	1027.61	1026.18	1024.99	1037.63	1033.81	1032.34	0.9899	0.9151	0.8555	1.0560	0.9861	0.9141	1546.61	1550.51	1555.42	1557.11	1561.05	1563.65
0.25	1032.74	1030.58	1029.16	1042.51	1039.21	1038.61	0.9844	0.9091	0.8490	1.0499	0.9811	0.9096	1551.32	1555.36	1560.18	1561.82	1565.87	1568.43
0.30	1037.83	1036.12	1034.97	1046.71	1044.91	1043.18	0.9788	0.9041	0.8446	1.0439	0.9762	0.9038	1556.04	1560.20	1564.96	1566.54	1570.71	1573.19
Potassium bromide + aqueous D-glucose solution																		
0.00	1005.60	1005.01	1004.57	1012.31	1010.62	1008.13	0.9685	0.8832	0.8032	1.0343	0.9377	0.8467	1527.31	1531.96	1536.09	1538.31	1541.63	1544.58
0.05	1012.18	1010.28	1009.98	1024.77	1022.98	1020.56	0.9915	0.9254	0.8622	1.0580	0.9791	0.9068	1531.98	1535.83	1540.28	1542.76	1545.55	1548.34
0.10	1017.36	1015.59	1015.31	1029.96	1028.07	1025.78	0.9890	0.9229	0.8598	1.0556	0.9765	0.9043	1536.08	1539.75	1544.14	1546.86	1549.47	1552.36
0.15	1022.69	1020.95	1020.47	1035.05	1033.23	1031.00	0.9865	0.9204	0.8568	1.0529	0.9739	0.9017	1540.29	1543.66	1548.02	1551.06	1553.41	1556.36
0.20	1028.08	1026.29	1025.76	1040.38	1038.47	1036.24	0.9840	0.9177	0.8541	1.0505	0.9713	0.8991	1544.42	1547.59	1551.86	1555.31	1557.33	1560.47

0.25	1033.27	1031.78	1030.12	1045.44	1043.68	1041.39	0.9812	0.9152	0.8505	1.0478	0.9686	0.8962	1548.57	1551.53	1555.72	1559.70	1561.26	1564.60
0.30	1038.68	1036.62	1034.34	1050.82	1048.54	1046.61	0.9785	0.9119	0.8467	1.0453	0.9655	0.8934	1552.73	1555.44	1559.60	1564.22	1565.17	1568.71
Potassium iodide + aqueous D-glucose solution																		
0.00	1005.60	1005.01	1004.57	1012.31	1010.62	1008.13	0.9685	0.8832	0.8032	1.0343	0.9377	0.8467	1527.31	1531.96	1536.09	1538.31	1541.63	1544.58
0.05	1017.29	1014.50	1012.35	1047.86	1043.95	1040.67	0.9931	0.8975	0.8085	1.0766	0.9754	0.8855	1530.48	1534.17	1539.02	1540.47	1544.07	1547.63
0.10	1022.36	1019.83	1017.64	1052.43	1049.18	1045.58	0.9877	0.8922	0.8034	1.0710	0.9705	0.8805	1533.99	1537.70	1542.55	1543.98	1547.57	1551.14
0.15	1027.58	1025.10	1022.76	1057.22	1054.45	1051.03	0.9827	0.8871	0.7981	1.0654	0.9655	0.8757	1537.51	1541.22	1546.06	1547.49	1551.08	1554.66
0.20	1032.87	1030.21	1028.07	1062.01	1059.63	1056.07	0.9777	0.8818	0.7924	1.0599	0.9597	0.8706	1541.02	1544.73	1549.58	1551.01	1554.60	1558.17
0.25	1038.18	1035.67	1033.31	1067.14	1065.06	1061.24	0.9723	0.8766	0.7866	1.0533	0.9542	0.8639	1544.34	1548.26	1553.11	1554.53	1558.11	1561.69
0.30	1043.45	1040.32	1038.43	1071.93	1070.30	1066.41	0.9669	0.8705	0.7813	1.0477	0.9484	0.8580	1548.07	1551.80	1556.62	1558.04	1561.63	1565.22

Table 2 Values of adiabatic compressibility (β) and molal hydration number (n_H) of alkali metal halides in aqueous D-glucose solution at different temperatures

Molality (mol.kg ⁻¹)	$\beta / (\times 10^{-10}\text{m}^2\text{N}^{-1})$						n_H					
	0.2 m			0.4 m			0.2 m			0.4 m		
	Temperature (K)											
	303.15	308.15	313.15	303.15	308.15	313.15	303.15	308.15	313.15	303.15	308.15	313.15
Sodium chloride + aqueous D-glucose solution												
0.00	4.2	4.2	4.2	4.1	4.1	4.1	-	-	-	-	-	-
	630	397	188	744	634	578						
0.05	4.2	4.1	4.1	4.1	4.1	4.1	5.22	5.18	5.16	4.83	4.59	4.82
	216	987	782	355	266	191	43	85	36	72	58	93
0.10	4.1	4.1	4.1	4.0	4.0	4.0	5.10	4.91	5.02	4.75	4.77	4.77
	820	622	399	980	869	814	92	31	63	92	68	31
0.15	4.1	4.1	4.1	4.0	4.0	4.0	5.07	4.85	4.79	4.73	4.73	4.77
	423	248	059	602	495	431	42	29	15	61	58	60
0.20	4.1	4.0	4.0	4.0	4.0	4.0	5.04	4.81	4.77	4.72	4.72	4.75
	028	876	688	226	119	056	81	87	48	10	43	31
0.25	4.0	4.0	4.0	3.9	3.9	3.9	4.99	4.79	4.64	4.71	4.72	4.69
	648	506	365	849	741	700	96	40	53	67	37	34
0.30	4.0	4.0	4.0	3.9	3.9	3.9	4.97	4.77	4.54	4.70	4.67	4.63
	264	137	045	477	383	350	07	26	75	03	80	65
Potassium chloride + aqueous D-glucose solution												
0.00	4.2	4.2	4.2	4.1	4.1	4.1	-	-	-	-	-	-
	630	397	188	744	634	578						
0.05	4.2	4.1	4.1	4.1	4.1	4.1	6.35	6.26	5.68	7.28	6.57	6.12
	126	902	741	158	107	087	52	68	16	57	85	90
0.10	4.1	4.1	4.1	4.0	4.0	4.0	6.20	5.82	5.10	6.27	5.86	5.69
	647	479	387	736	695	666	08	03	15	50	13	78
0.15	4.1	4.1	4.0	4.0	4.0	4.0	5.89	5.46	5.16	6.04	5.71	5.55
	229	104	972	286	261	244	02	46	26	80	19	30
0.20	4.0	4.0	4.0	3.9	3.9	3.9	5.77	5.37	5.00	5.92	5.62	5.47
	798	702	614	840	830	826	32	14	99	13	53	10
0.25	4.0	4.0	4.0	3.9	3.9	3.9	5.67	5.34	4.86	5.75	5.38	5.37
	378	288	278	431	477	426	92	63	73	77	29	70
0.30	4.0	4.0	3.9	3.9	3.9	3.9	5.45	5.04	4.72	5.59	5.31	5.31
	032	010	960	046	078	025	79	04	86	30	22	36
Potassium bromide + aqueous D-glucose solution												
0.00	4.2	4.2	4.2	4.1	4.1	4.1	-	-	-	-	-	-
	630	397	188	744	634	578						
0.05	4.2	4.1	4.1	4.0	4.0	4.0	7.08	7.69	6.37	9.42	9.47	9.19
	068	790	687	986	874	841	38	02	05	80	41	90
0.10	4.1	4.1	4.1	4.0	4.0	4.0	6.50	6.53	6.21	7.54	7.58	7.41
	598	366	212	532	418	391	83	88	51	43	70	72
0.15	4.1	4.0	4.0	4.0	3.9	3.9	6.30	6.36	6.09	6.86	6.90	6.77
	129	892	753	088	975	952	87	06	37	97	11	00
0.20	4.0	4.0	4.0	3.9	3.9	3.9	6.19	6.07	6.02	6.53	6.56	6.45
	664	478	296	643	527	510	56	90	40	43	97	72
0.25	4.0	4.0	3.9	3.9	3.9	3.9	6.09	5.84	5.87	6.29	6.31	6.21
	215	091	881	214	103	091	19	60	85	83	61	48
0.30	3.9	3.9	3.9	3.8	3.8	3.8	6.02	5.81	5.65	6.14	6.15	6.05
	763	641	523	778	671	670	24	95	39	82	80	06
Potassium iodide + aqueous D-glucose solution												
0.00	4.2	4.2	4.2	4.1	4.1	4.1	-	-	-	-	-	-
	630	397	188	744	634	578						
0.05	4.1	4.1	4.1	4.0	4.0	3.9	10.4	10.7	10.2	20.2	20.0	20.2
	803	548	384	114	023	957	190	469	269	663	887	255
0.10	4.1	4.1	4.0	3.9	3.9	3.9	8.54	8.12	7.76	13.7	13.4	13.5
	275	115	969	536	487	403	68	62	28	416	023	875
0.15	4.0	4.0	4.0	3.9	3.8	3.8	7.90	7.68	7.23	11.1	10.9	10.7
	749	579	484	049	993	994	49	10	57	792	835	581

0.20	4.0	4.0	3.9	3.8	3.8	3.8	7.62	7.40	7.32	9.81	9.66	9.61
	212	059	888	588	533	500	02	60	27	56	99	00
0.25	3.9	3.9	3.9	3.8	3.8	3.8	7.45	7.21	6.88	9.03	8.86	8.81
	675	550	484	112	083	050	31	76	98	99	25	58
0.30	3.9	3.9	3.8	3.7	3.7	3.7	7.28	7.02	6.86	8.51	8.40	8.44
	162	070	954	638	589	519	39	57	14	10	79	61

Table 3 Values of apparent molal compressibility (β_k) and apparent molal volume (β_v) of alkali metal halides in aqueous D-glucose solution at different temperatures

Molality (mol.kg ⁻¹)	$-\Phi_k / (\times 10^{-8}\text{m}^2\text{N}^{-1})$						$-\Phi_v / (\text{m}^2\text{N}^{-1})$					
	0.2 m			0.4 m			0.2 m			0.4 m		
	Temperature (K)											
	303.15	308.15	313.15	303.15	308.15	313.15	303.15	308.15	313.15	303.15	308.15	313.15
Sodium chloride + aqueous D-glucose solution												
0.05	12.6	12.0	11.8	12.4	12.1	11.9	101.5	91.08	88.33	111.1	114.9	100.5
	257	554	409	230	590	181	728	52	79	730	211	243
0.10	12.5	11.9	11.7	12.1	11.9	11.8	103.2	99.04	90.52	107.0	104.2	101.1
	050	483	077	147	948	431	633	53	81	241	346	195
0.15	12.4	11.8	11.5	12.0	11.9	11.8	103.5	99.97	95.10	106.3	104.1	100.4
	655	959	355	532	295	235	616	40	69	655	686	582
0.20	12.4	11.8	11.4	11.9	11.8	11.7	103.1	99.94	94.36	103.6	102.5	99.82
	088	421	793	158	454	623	638	09	03	160	525	99
0.25	12.3	11.7	11.2	11.8	11.8	11.7	103.0	98.96	94.74	103.1	102.2	100.8
	238	590	896	884	309	060	445	57	86	913	952	417
0.30	12.2	11.6	10.9	11.8	11.6	11.6	101.8	98.18	90.69	102.7	100.7	101.7
	325	963	691	464	986	569	711	30	38	105	714	477
Potassium chloride + aqueous D-glucose solution												
0.05	15.0	14.1	13.0	18.7	16.9	15.6	116.2	99.42	96.68	167.8	154.0	140.7
	483	120	069	285	711	745	743	732	361	591	890	809
0.10	14.5	13.4	12.2	15.6	14.7	14.1	111.6	100.6	101.7	134.4	127.4	121.9
	915	460	995	961	002	884	005	213	608	701	717	341
0.15	14.0	12.9	12.1	15.0	14.1	13.7	110.9	102.8	95.68	128.1	119.7	116.9
	732	842	427	715	420	542	044	767	816	479	207	744
0.20	13.8	12.9	12.0	14.7	13.6	13.3	109.3	105.2	100.1	124.9	110.6	110.6
	237	395	914	378	274	629	630	482	179	869	503	757
0.25	13.6	12.7	11.5	14.2	13.3	13.2	107.8	102.0	91.66	119.2	113.0	110.9
	081	596	081	322	369	219	813	144	653	574	845	832
0.30	13.0	12.1	11.2	13.7	13.1	13.0	103.7	99.39	90.94	113.1	111.9	109.6
	843	705	641	198	807	679	113	415	317	986	367	011
Potassium bromide + aqueous D-glucose solution												
0.05	16.8	16.5	14.5	25.4	25.3	24.5	130.7	104.7	107.5	246.0	244.4	235.3
	223	857	496	392	809	266	488	562	893	521	846	675
0.10	15.3	14.7	14.2	19.3	19.3	18.8	116.8	105.1	106.7	174.2	172.5	167.5
	020	714	595	956	425	355	268	542	936	362	485	191
0.15	14.8	14.5	14.0	17.2	17.2	16.8	113.1	105.6	105.3	149.6	147.5	144.3
	342	142	143	895	058	392	805	185	993	389	144	078
0.20	14.5	14.0	13.9	16.2	16.2	15.9	111.6	105.7	105.3	138.5	136.1	134.0
	918	776	047	693	049	136	557	512	496	257	847	412
0.25	14.3	13.6	13.5	15.5	15.4	15.1	109.9	103.6	101.6	130.7	127.9	125.9
	507	151	152	824	521	865	453	020	166	910	620	768
0.30	14.2	13.5	12.8	15.1	15.0	14.7	109.5	103.7	94.51	126.6	123.6	121.3
	285	840	683	757	243	360	343	280	573	881	347	279
Potassium iodide + aqueous D-glucose solution												
0.05	26.4	24.9	22.5	60.1	59.6	59.2	232.3	188.6	154.7	659.5	659.4	645.3
	488	713	983	358	887	430	329	887	269	154	308	870
0.10	20.6	19.0	17.6	38.6	37.3	37.2	166.5	147.2	129.9	396.1	381.3	373.1
	525	618	651	173	567	581	016	960	414	573	837	007
0.15	18.7	17.7	16.4	30.3	29.6	29.0	145.5	133.1	120.5	295.5	288.9	283.5
	467	628	465	097	400	129	522	005	498	952	652	289
0.20	17.8	16.9	16.3	26.0	25.5	25.2	135.4	125.2	115.8	245.3	242.3	237.2
	658	967	874	221	948	539	256	067	545	142	107	551
0.25	17.3	16.5	15.7	23.5	23.2	23.1	129.4	121.8	117.0	216.4	216.0	216.5
	405	533	543	661	035	144	292	635	590	890	990	137
0.30	16.9	16.0	15.5	21.8	21.6	21.5	125.2	116.9	112.1	196.1	195.6	192.5
	028	486	105	752	328	335	990	481	880	527	891	354

Table 4 Values of limiting apparent molar compressibility (ϕ_{κ}^0) and limiting apparent molar volume ($\phi_{V,L}^0$) their constant S_{κ} and S_V of alkali metal halides in aqueous D-glucose solution at different temperatures

Alkali metal halides	Molality (mol.kg ⁻¹)	ϕ_{κ}^0 ($\times 10^{-8}$ m ² N ⁻¹)			S_{κ} ($\times 10^{-8}$ N ⁻¹ m ¹ mol ⁻¹)			$\phi_{V,L}^0$ ($\times$ m ³ mol ⁻¹)			S_V ($\times 10^{-8}$ N ⁻¹ m ¹ mol ⁻¹)		
		303.15	308.15	313.15	303.15	308.15	313.15	303.15	308.15	313.15	303.15	308.15	313.15
NaCl	0.2	12.8847	12.2991	12.4635	1.1337	1.0729	2.4604	102.3352	-90.4624	-87.1755	-1.0182	-18.3396	-12.6844
	0.4	12.7313	12.4318	12.1018	1.7121	1.2929	0.7848	116.1554	119.8069	100.0519	25.9497	37.1161	-1.7380
KCl	0.2	16.3784	15.2153	14.0589	5.7976	5.3182	4.9716	123.4870	-99.7150	105.0160	33.5198	-4.6622	21.9794
	0.4	20.9679	18.7763	16.9549	13.8813	11.0236	7.6217	191.9361	173.2236	155.5502	150.1594	124.8473	91.8025
KBr	0.2	18.0556	18.0726	15.7285	7.51570	8.7889	4.6485	139.8142	106.2481	117.2331	60.6894	3.6656	33.9109
	0.4	30.2861	30.3121	29.1882	29.9602	30.2476	28.5254	301.2999	300.9856	288.5451	347.5819	352.4196	331.4234
KI	0.2	30.7931	28.6676	25.3167	27.5795	25.0243	19.6271	280.7197	222.6654	173.7690	309.5608	207.6279	120.6796
	0.4	78.9403	77.7396	77.1122	112.7615	111.1944	110.3425	884.8792	874.0594	853.0065	1362.4926	1346.1540	1308.6820

Table 5 Values of partial transfer volume ($\Delta\phi_{V^0}$), A and B co-efficient of Jones – Dole equation of alkali metal halides in aqueous D-glucose solution at different temperatures

Alkali metal halides	Molality (mol.kg ⁻¹)	Partial transfer volume ($\Delta\phi_{V^0}$)			A (dm ³ mol ^{-3/2})			B (dm ³ mol ⁻¹)		
		303.15	308.15	313.15	303.15	308.15	313.15	303.15	308.15	313.15
NaCl	0.2	-11.8040	-2.9898	15.2459	0.0020	0.0022	0.0071	0.3223	0.3322	0.3566
	0.4	-25.6242	-32.3343	2.3695	0.0130	0.0162	0.0461	0.2884	0.2957	0.2481
KCl	0.2	0.7653	16.5449	26.5368	0.2551	0.3449	0.5333	0.4487	-0.5763	-0.8437
	0.4	-67.6838	-56.9637	-23.9974	0.2277	0.4302	0.6078	0.3988	-0.6821	-0.9300
KBr	0.2	18.3010	26.3239	45.7081	0.1563	0.3003	0.4580	0.2624	-0.4617	-0.6879
	0.4	143.1847	168.4086	125.6039	0.1501	0.2778	0.4382	0.2501	-0.4289	-0.6494
KI	0.2	101.3465	-43.2525	5.6565	0.1814	0.1315	0.0803	0.3503	-0.2964	-0.2432
	0.4	705.5060	694.6465	673.5810	0.2750	0.2727	0.3104	0.4797	-0.4792	-0.5427

From Table 1, one can notice that in all the four alkali metal halide systems which were taken for study, the values of density increases with increase in concentration of metal halides as well as aqueous D-glucose content (0.2 mol Kg⁻¹ and 0.4 mol Kg⁻¹) and the same decreases with change of temperature. But however the ultrasonic velocity found to be increasing with increase in concentration of alkali metal halides and the content of aqueous D-glucose as well as with rise in temperature. Such an observed increase in the ultrasonic velocity values which suggests that disruption of water structure is enhanced with the addition of solvent (aqueous D-glucose solution) and the solutes (alkali metal halides). Moreover, the increase in ultrasonic velocity in these solutions further be attributed as the cohesion brought about the ionic

hydration.

Incidentally, the density (ρ) which is a measure of solvent-solvent and ion-solvent interactions. Increase of density with concentration indicates the increase in solvent-solvent and solute-solvent interactions, whereas the decrease in density indicates the lesser magnitude of solute-solvent and solvent-solvent interactions. Increase in density with concentration is due to the shrinkage in the volume which in turn is due to the presence of solute molecules. In other words, an increase in density may be interpreted to the structure-maker of the solvent due to the added solute and the decrease in density with concentration indicates structure-breaker of the solvent [27]. However, our present investigation finds that the increase in density and ultrasonic velocity with rise in temperature

suggest that decrease in intermolecular forces due to increase in thermal energy of the system.

The perusal of Table 2 exhibits the values of adiabatic compressibility (β), which are found to be decreased with increase in molal concentration of solutes and content of D-glucose as well as rise in temperature. Such a decrease in adiabatic compressibility observed in this alkali metal halide with aqueous D-glucose in the present system clearly confirms the conclusions drawn from the ultrasonic velocity data. It is well known fact that when a solute dissolves in a solvent, some of the solvent molecules are attached to the ions (produced from the solutes), because of ion-solvent interaction. Since, the solvent molecules are oriented in the ionic field

(ie electrostatic field of ions $-\text{CH}_2\text{OH}$ and CHO). The solvent molecules are more compactly packed in the primary solvation shells as compared to the packing in the absence of the ions. This is the reason, why the solvent is compressed by the introduction of the ions. Thus, the electrostatic field of the ions causes the compression of the medium giving rise to a phenomenon called 'Electrostriction'. Since the water molecules are compressed, they do not respond to a further application of pressure. So the solutions become harder to compress. This will lead to the decrease in compressibility values. This may further ascribed that such a decrease in adiabatic compressibility (β) is attributed to the influence of the electrostatic field of ions (Na^+ , Cl^- , K^+ , Br^- , I^- ...etc) on the accompanying molecules. It may be inferred that weakening of hydrogen bond strength formed by the solute and solvent molecules may also be the reason for decrease in compressibility.

The hydration number that usually reflects the electrostriction effect of the alkali metal halides in the vicinity of the water molecules. From Table 2, one can observe that the values of n_H are positive in all the four liquid systems studied and such positive values of n_H indicate an appreciable solvation of solutes [28]. It can be taken as an added support for the structure making nature of solutes as well as the presence of dipolar interactions between the solutes and water molecules. This parameter also suggests that the compressibility of the solution will be less than that of the solvent, resulting in solutes will gain more mobility and have a more probability of contacting solvent molecules. This may enhance the interaction between the solute solvent molecules. Our present study shows that the values of n_H which are decreasing with increasing molal concentration of solutes (alkali metal halides) and content of D-glucose as well as rise in temperature. The decreasing value of n_H suggest that an enhancement of solute- co-solute interactions. Further the decreasing values of n_H with rise in temperature clearly indicates that the strength of the interactions get weakened among the solute- solvent molecules.

It can be qualitatively ascribed that, when the alkali metal halides are dissolved in water + D-glucose mixtures, the water molecules are attached to the ions strongly to the electrostatic forces, which introduce a greater cohesion in the solutions [29] resulting the increasing of cohesion, whenever an increase of metal halide concentration in the solution. Such an increased association observed in the solution may also be due to the water structure enhancement brought about by the increased electrostriction in the presence of D-glucose. Similar effect was reported by earlier workers [30].

Molal compressibility and volume studies:

The following observations from Table 3 noticed by the authors on apparent molal compressibility (ϕ_k) and apparent molal volume (ϕ_v) of alkali metal halides namely NaCl, KCl, KBr and KI in aqueous D-glucose solution at 303.15, 308.15 and 313.15 K which are listed as:

- The values of ϕ_k and ϕ_v are all negative over the entire range of molality of solutes as well as solvent.
- In the present study, it is observed that the values of ϕ_k and ϕ_v which are found to be increased with increase in molal concentration of solute (alkali metal halides) and rise in temperature, and however the same found to be decreased with increase in molal concentration of solvent (aqueous D-glucose solution).
- Our present study also observes that the maximum value of ϕ_k and ϕ_v recorded for NaCl system which indicates that molecular interaction is more pronounced in that system.

Further, from Table 3, the magnitude of ϕ_k and ϕ_v , the molecular interaction is of the order $\text{NaCl} > \text{KCl} > \text{KBr} > \text{KI}$.

All the above observation clearly shows that the solute – solvent interactions taking place in all the four liquid systems. The negative values of ϕ_k and ϕ_v indicates hydrophilic interactions occurring in these systems. As more number of water molecules is available at lower concentration of metal halides, the chances for the penetration of solute molecules in the solvent mixtures are highly favored [31]. Our present decreasing trend of ϕ_k and ϕ_v values with increasing molal concentration of aqueous D-glucose content reveals that the weakening solute – solvent interactions in the mixtures.

The evaluated parameter limiting apparent molal compressibility (ϕ_k^0) which provide informations regarding the ion – solvent interactions and its related constant (S_k) of the ion – ion interaction in the solution, which are systematically tabulated in Table 4. The authors noticed that the values of ϕ_k^0 negative in all the systems and decreases with increasing concentration of the solute as well as the aqueous D-glucose content (except in the first system, where it is found to be increased) and the same increases with change of temperature. The magnitude of negative values of ϕ_k^0 is higher in NaCl system suggesting that the presence of strong ion – solvent interactions, which are more pronounced in this system comparing the other. This once again supports our earlier conclusion. Generally, the decreasing values of ϕ_k^0 with elevation of temperature shows that the weakening of ion – solvent interactions in the solution. Its related constant (S_k) whose values are positive in all the four systems studied. These are tabulated in Table 4. From this tabulation, one can notice that the values of S_k increases with increasing molal concentration of solutes (metal halides) and aqueous D-glucose content. The increasing trend in the solution attributing the presence of ion – ion interaction of the solution. However the same found to be decreased with the elevation of temperature suggesting the weakening of ion – ion interactions in the liquid mixtures.

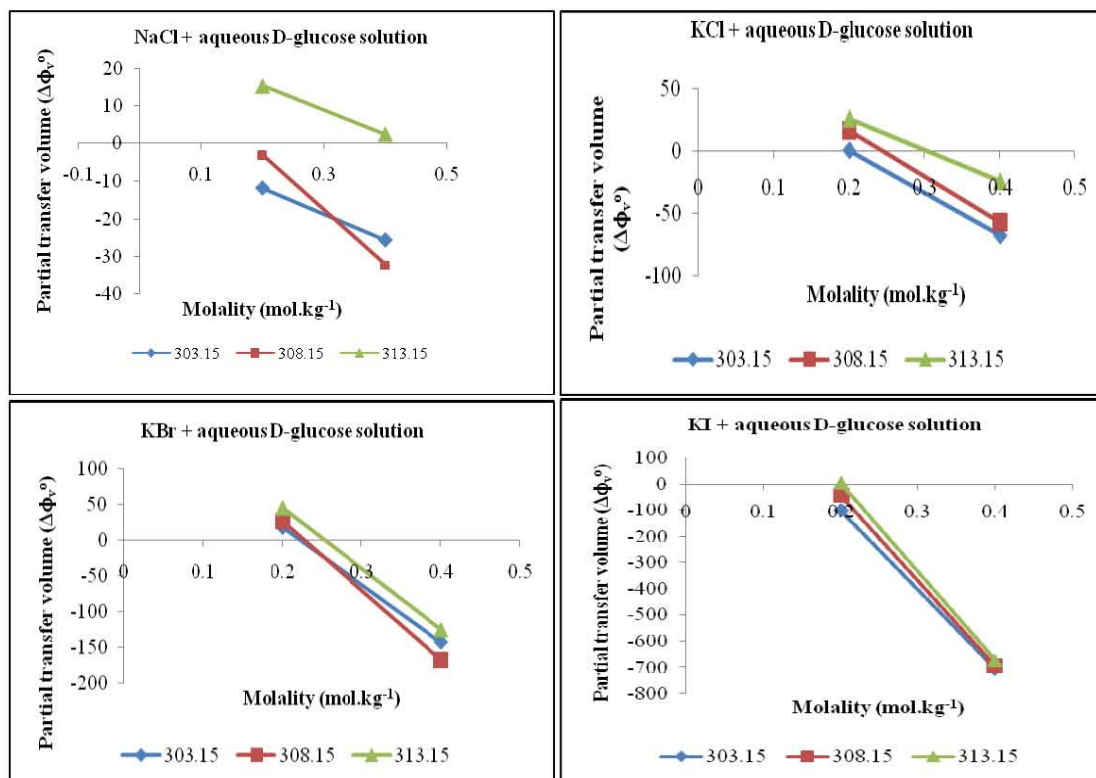
The perusal of Table 4 represents the values of limiting apparent molal volume (ϕ_v^0) which are exhibiting the positive values in all the four liquid systems studied.(Except in NaCl system, in which the values are negative at lower molality and becomes positive at higher molality of the solvent content) and decrease with increase in molal concentration of solutes (alkali metal halides) and content of solvent (aqueous D-glucose solution).However, the same is found to be increased with the rise of temperature. This may

enhance/reduce electrostriction of water molecules. The negative values of ϕ_v^0 for the systems indicate the existence of smaller solute-solute interactions. Further, the decrease in ϕ_v^0 for alkali metal halides indicate the solute-solute interactions decreasing with increase of aqueous D-glucose content. Further, the increasing trend of limiting apparent molal volume values with the elevation of temperature too suggests the weakening of solute-solute interaction. The values of S_v are reported in Table 4 which are all negative in all

the four systems studied. The negative values of S_v indicate the presence of solute-solute interaction and less complex ion formation taking place in the systems. For saccharide, the values of S_v increases with increasing concentration of alkali metal halides which indicate the decreased solute-solute interaction present in the mixture.

Partial transfer volume studies:

Fig. 1 Values of partial transfer volume ($\Delta\phi_v^0$) with molality of aqueous D-glucose solution at different temperatures



The co-sphere overlap model [32] can be utilized to rationalize the partial transfer volume values ($\Delta\phi_v^0$) in terms of solute-co – solute interactions. Our present study shows that the value of partial transfer volume of alkali metal halides in aqueous D-glucose solution are all almost negative and (from Fig 1) they become non-linear with increase in concentration of the solutes (alkali metal halides) as well as aqueous D-glucose content. The non-linear behavior of $\Delta\phi_v^0$ values indicates weakening of interactions between the D-glucose and co-solutes (NaCl/ KCl/ KBr/ KI). Based on this model, the transfer volume $\Delta\phi_v^0$ can be interpreted that ions of co – solute and D-glucose comes into play because of the interactions between

- ions of co-solutes (NaCl/ KCl/ KBr/KI) and hydrophobic, - OH sites of saccharide molecules and
- ions of co-solutes and hydrophilic parts/groups of the saccharide molecules.

From our present investigation, we realized the feasibility of former type of interaction contributes the non-linear behavior between solutes and co – solutes and there is no feasibility for the existence of second type of interactions. Further the non-linear

nature of the $\Delta\phi_v^0$ values over the rise of temperature clearly supporting our above cause. Hence, it may be presumed from the $\Delta\phi_v^0$ values studied, the hydrophobic-ionic interactions dominate over hydrophilic-ionic interactions in the present study.

Viscometric Studies:

Viscosity is another important parameter in understanding the structure as well as molecular interactions occurring in the solutions. From Table 1, the values of viscosity decreases with increasing molal concentration of solutes and aqueous D-glucose content, whereas a reverse trend is observed in NaCl system. But however, the same is found to be decreased with increase of temperature. This increasing or decreasing trend indicates the presence of molecular interactions occurring in these systems. In order to shed more light on this, role of viscosity B-coefficient has also been obtained. From Table 5, it is observed that the values of A are almost positive in all the systems. (Except in NaCl, where the values are negative at lower molality and becomes positive at higher molality of the solvent). Since A is a measure of

ionic interactions [33], this behaviour shows the existence of strong ion-ion interactions prevailing in NaCl system comparing the other three systems.

Further, B-coefficient which is also known as a measure of order or disorder which is introduced by solute with the solvent molecules. It is also measure of ion-solvent interactions in the liquid mixtures. In our present study, the B-values are positive in NaCl system and are negative in all the remaining systems. The positive values of B may be ascribed to the increased ion-solvent interactions owing to the structure-making tendency of the D-glucose molecules. The positive values of B-coefficient clearly suggest that the existence of strong ion – solvent interaction. Hence, a strong molecular interaction is found to exist in NaCl system comparing the other three liquid systems. The decreasing behaviour of viscosity values with rise of temperature clearly establishes the weakening of ion – solvent interaction in the solvent mixture.

Hence, it is very obvious that our present investigation clearly establishes the molecular interactions are more pronounced in NaCl system comparatively with other three systems and such interactions are of the order: NaCl > KCl > KBr > KI.

CONCLUSION

In the present investigation, density, viscosity and ultrasonic velocity data have been measured for alkali metal halides in aqueous D-glucose solution at 303.15, 308.15 and 313.15 K and their acoustical parameters have been applied to explore the possible molecular interaction existing in the present system of mixtures. From the trends and behaviour of acoustical parameters, the authors have summarized their investigations as follows,

- A very weak molecular interionic interactions such as solute-solvent, ion-ion, ion-solvent, solute-solute, solute-solvent etc., are generally observed in the present systems of liquid mixtures.
- Our viscometric study also diagnoses that a weak ion-ion and ion-solvent interactions are existing in the present study.
- The trends of our partial transfer volume values which predicts about the interactions between the solute and the co-solute suggesting that the hydrophobic-ionic interactions dominate over hydrophilic-ionic interactions.
- The elevation of temperature in the present study may play a vital tool for weakening of the molecular association between the solutes (alkali metal halides) and solvent (D-glucose solution).
- Of all the liquid systems taken for study, the molecular associations are more pronounced in NaCl System comparing the other systems.
- The molecular interaction among the present liquid systems studied are of the order: NaCl > KCl > KBr > KI.

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